

ART I.—*The Roasting and Treatment by Chlorine of
Gippsland Auriferous Ores.*

By D. CLARK, B.C.E.

[Read 10th March, 1898.]

The chlorination plant at the Bairnsdale School of Mines was erected with the dual object of serving as a testing plant and as a means for training students in the treatment of complex ores on a considerable scale.

The inclined long-hearth reverberatory furnace for roasting and the Plattner system for chlorinating were adopted after consultation with Mr. Henry Rosales, M.E., as the best for illustrating in detail the various operations essential for successful treatment. The principal dimensions of the furnace are :—

Length of roasting hearth, 35ft. 6in.

Width, 4ft. 2in.

Height of centre of arch above hearth, 1ft. 11in.

Rise of arch, 4in.

Width of fireplace, 2ft.

Height of bridge, which is hollow and has air-holes at the level of the hearth above the firebars, 1ft. 6in., and 1ft. above hearth.

Slope of hearth, 1 in 9, with six rabbling doors, 13in. by 9in.

Owing to some misunderstanding when being built, the height of the roof above the hearth of the furnace was too great, and, though roasting may be satisfactorily performed and a temperature much higher than is necessary be obtained, a greater consumption of fuel is entailed, owing to the larger volume of air passing into the furnace and the greater distance of the roof from the hearth.

The auriferous ores which have been treated consisted usually of sulphides and sulpharsenides, together with heavy oxides concentrated either at our own works or in the district from which they came.

The following list will indicate the commoner minerals, and also serve to show the standard of the gold contained :—

District.	Metallic minerals in order of relative abundance.	Standard of gold per 100.
Mallacoota ...	Limonite, pyrite, bismutite	96
Bemm River ...	Arsenopyrite, pyrite, galena, blende ...	85
Mount Tara ...	Pyrite, limonite, barytes	80
Mount Wills ...	Pyrite, stibnite, arsenopyrite, argen- tite, cerargyrite	66 to 76
Cassilis	Arsenopyrite, blende, pyrite, galena ...	66 to 80
Haunted Stream	Arsenopyrite, pyrite, galena, blende ...	90 to 96
Deptford	Do. do. do.	96
Bullumwaal ...	Arsenopyrite, pyrite, galena, blende, and wad	70 to 95
Grant	Arsenopyrite, pyrite, galena, blende, and wad	96
Dargo	Arsenopyrite, pyrite, galena, blende, wad, and erythrite	96
Budgee	Arsenopyrite, pyrite, galena, blende, chalcopyrite	82
Walhalla	Arsenopyrite (needle pyrites), pyrite, bournonite, galena, blende	82
Wood's Point ...	Pyrite, arsenopyrite, stibnite, siderite	82 to 97

As a general rule, from 1 to 5 per cent. of concentrates is obtained from raw ore, yet in the case of the Cassilis lodes the percentage of metallic mineral contents may rise to 50 per cent. Parcels of concentrates from Glen Wills have contained 25 ozs. gold and 90 ozs. silver per ton, yet the usual returns, when crushing from ounce stone, will be from 2 to 5 ozs. per ton of concentrates.

The gold in the ore is an alloy of gold and silver, containing from 66 per cent. of gold to 97 per cent. in the highest grades; only very minute quantities of copper, iron, lead and bismuth are to be detected. Copper is certainly a natural alloying element, but iron and lead are probably oxides or sulphides mechanically mixed only.

As Mr. Howitt pointed out, the gold ratio is invariably higher when occurring in sedimentary formations than when associated with granites or diorites.

The separate parcels of ore are weighed and samples are taken and dried at 110° C., and carefully assayed. The total weight and value of each lot is thus determined. The ores are then blended according to their composition, care being taken to

keep pyrites in excess of arsenical ores, and largely in excess of antimony sulphides; blanket sand, containing a large amount of silica, serves to dilute the concentrated pyrites.

The mixture should be dried before introducing it into the furnace, otherwise it will be difficult to screen; and if damp lumps of ore pass in, these will be difficult to roast, since they do not break up and thus pass through the furnace unaltered. By screening through a sieve, containing 4 holes per linear inch, all scraps of iron, lumps of semi-oxidised ore and other injurious materials are eliminated, and the fine material is run through a hopper and spread out upon the floor in a layer about 4 inches deep. Since a perfect oxidising roast is needed, it follows that to perform this operation quickly, a copious supply of warm air is needed, and reducing gases should be excluded. On the other hand, if the upper end of the furnace containing the raw sulphides becomes too hot, these burn and generate a large amount of heat; if this action is not moderated, fusion cannot be prevented, and the sulphides are rendered practically unfit for subsequent treatment. If the temperature is rising too rapidly the air must be shut off, or raw blanket sand fed in until conditions are normal.

Free sulphur, sulphides of arsenic, and metallic arsenic sublime and pass into a current of air about 2 inches above the surface of the ore, where they burn with a characteristic livid flame, while underneath may be seen a conspicuous, wavy, brick-red flame, which I assume to be due to the colour of the volatilised sulphur and sulphides of arsenic. As soon as these reactions go on freely the ore is mobile, and when stirred will run like a liquid, since the various particles are buoyed up on a cushion of sublimed products.

The ore is stirred vigorously at this stage, and after all sublimation products have disappeared, it is moved on to the next hearth.

Opposite the second door the flame is emitted from the surface of the ore itself, yet the mass will scintillate brightly, if stirred; the rabbling is carried on at this stage as continuously as possible, since a large percentage of sulphur is eliminated by oxidation.

The same material, when moved to the next door, will only sparkle when dropped through a layer of hot air, and if left unstirred for any length of time a soft crust forms, which

ultimately penetrates the mass; sulphur at this stage is mainly eliminated, and the material may be thrown into wave-like ridges to expose as large a surface as possible to the air. When moved to the fourth door, no sparks may be seen on stirring, but the ore appears to be porous and offers resistance to the rabbling tools.

When opposite the fifth door the ore is only stirred occasionally, since the sulphides have practically disappeared, and all that remains to be done is to decompose any sulphate of iron formed, or to oxidise the magnetic oxide to the higher state.

After this the ore is moved down to the hottest part of the furnace, or next to the fire-bridge, care being taken to exclude reducing gases at this stage; a few minutes' exposure on this hearth is generally sufficient to decompose any injurious sulphates and to raise the whole of the iron to its highest state of oxidation. Should it be kept too long on this hearth, especially in the presence of silica, it is again reduced to the magnetic form, and afterwards will partly unite with silica to form a black sintery mass from which it is difficult to extract the gold. The temperature should on no account reach the melting point of the bullion to be treated, otherwise the gold will be transformed from a porous, spongy, well annealed state, in a condition readily attacked by chlorine, to a spherical form offering but little surface to be acted on. Another danger is that, in the case of limonite ores, which, though they open up and lose their combined water at a calcining temperature, yet, at too high a temperature, the mass closes again and seals up the contained gold.

Should the ore contain much zinc, arsenic, or antimony, or low grade bullion, the introduction of a small quantity of salt is beneficial on the last hearth; it has been found that from 5 to 10 lbs. is sufficient for a ton of ore, and if introduced and stirred vigorously into the ore, when heated up to about 800° C., all ferrous oxide is converted almost instantly into ferric oxide, while hydrochloric acid, chlorine, and volatile chlorides are given off in abundance; below this temperature no perceptible action goes on. The ore is discharged from the furnace almost immediately.

Samples taken all over the hearth, before introducing the salt and after withdrawing the ore from the furnace, show no losses of gold due to volatilisation. As a matter of fact, gold is very

slowly acted on by chlorine at a temperature of 800° C., while above that temperature it is more sensibly acted upon, and also at an increasing rate down to 300° C.

By continually attending to the furnace, it was found that the raw ore could be shifted from each hearth every 45 minutes, so that pyrites could be perfectly roasted in $4\frac{1}{2}$ hours; and, generally speaking, a better roast may be obtained in that time than by keeping the ore longer in the furnace.

In order to find out the state of the ore on the various hearths, samples were taken just before the material was moved downwards. Unfortunately, samples opposite doors 4 and 5 were mislaid; but, on testing the others with an ordinary horseshoe magnet, it was found that the material was highly magnetic from No. 1 door down to No. 3. Nearly all works¹ on roasting of ores state that pyrites loses one atom of sulphur, and the oxidation of the remaining atom is through the agency of sulphuric anhydride uniting with ferrous oxide to form a sulphate, which is afterwards decomposed into ferric oxide and sulphuric anhydride. Such, however, has not been the case in our furnace; in it, after the distillation of the free sulphur and arsenic products, the material left consists of magnetic sulphide; after contact with the air it becomes magnetic oxide of iron, and finally, by heating in the air alone, it is transformed into the sesqui-oxide.

The quantity of magnetic material in samples taken from No. 1 floor, 20 %; No. 2 floor, 24 %; No. 3 floor, 22.4 %, which contained only 5 % sulphur; No. 6 floor, .4 %, with no sulphur and no ferrous oxide. The quantity of sulphate of iron present at any stage was exceedingly minute, and, since the heat required for its decomposition was not reached before about the fifth hearth, it is plain that too much stress has been laid on Plattner's statement.

My present investigations show that very little sulphur is combined with the iron beyond the third floor of the furnace, and in order to more definitely establish what the main reactions are, samples are being collected from furnaces of various design for future testing.

¹ Roberts-Austin's Presidential Address to Chemical Section British Association, 1891; Peter's Modern American Methods of Copper Smelting, p. 170; Metallurgy of Gold, from Plattner's Metallurgische Röstprozesse, p. 231.—T. K. Rose; The Metallurgy of Gold.—Eissler, 4th edition, p. 207.

In samples Nos. 1, 2, 3 there is a large quantity of iron in the ferrous state; but in No. 6 there is none, although the oxide is slightly magnetic. Professor Liversidge has noticed this, and called attention to J. Robbin's¹ experiment of heating black magnetic oxide until it turns red, when it is found to be still magnetic.

Many misleading statements² have appeared concerning the reactions in roasting furnaces, but it appears that arsenic may be eliminated from any metal so long as sulphur is in excess, and thus there is but little difficulty in roasting any arsenical ores. Antimony ores are more troublesome, since a non-volatile oxide often forms, yet if pyrites is largely in excess the reducing action of the volatilised sulphur tends to prevent highly oxidised forms of antimony forming, and favours the expulsion of antimonious oxide in a volatile form.

Blende, up to 15 per cent., has not offered any difficulties, since it is non-volatile and infusible and oxidises mainly to a sulphate, which, if desired, may be leached out. Some is roasted to oxide, and since this is readily acted upon by acids, it may be transformed partly into chloride by the addition of salt. The heat should never be raised to such a temperature as to decompose zinc sulphate.

Galena roasts quietly to sulphate of lead; this, at a high temperature in contact with silica, will evolve sulphuric anhydride and glaze the silica with an impermeable coat of silicate of lead. When present in quantities up to 5 per cent., no trouble was experienced except when roasted with salt, when chloride of lead formed.

Bismuth oxide passes through the furnace unchanged.

Copper pyrites. These minerals never amounted to 1 per cent. of the ore put in the furnace, and in small quantities give no trouble; a mixture of sulphate and oxide remains even after roasting at a high temperature.

Manganese oxides pass through the furnace and give no trouble; the cobalt which the earthy ones contain is converted into a sulphate.

¹ Iron rust possessing magnetic properties, A.A.A.S., 1892.

² Wilson's Chlorinate Process.

Limonite evolves water and becomes spongy; but at too high a temperature it will contract.

Siderite evolves carbon dioxide and carbon monoxide, and becomes spongy ferric oxide.

The last three minerals should be treated by themselves on the last hearth of the furnace, since they require a temperature just sufficient to dehydrate them and render them fit for leaching.

Metallic iron is wholly oxidised if not in pieces over one-eighth of an inch diameter.

Barite passes through the furnace unchanged, and offers no difficulties.

When oxygen is supplied to ores in the manner suggested, there need not be any fear of antimoniates or arseniates interfering with subsequent work; nor would I recommend the addition of carbon to eliminate these. Some fine charcoal accidentally became mixed with a small parcel of roasted ore at our works, and it was found, in burning this out, that a great deal of ferric oxide became reduced to triferric tetroxide, which we could not convert back again into the higher form.

In order to test whether the material has been thoroughly roasted, several tests have been recommended. Kustel¹ recommends throwing the heated ore into water and then plunging a bright iron rod in; if the rod is darkened, then sulphates are still present.

Rose² has pointed out that this method is worthless, since it will not show the presence of sulphate of iron; he, however, suggests the addition of barium chloride as a test for sulphates. But this test is also valueless, since sulphate of zinc, or sodium, may exist in an ore without interfering with the action of chlorine; and when it is considered that sulphuric acid in certain cases is actually mixed with the ore, it is certainly not necessary to test specially for this.

Eissler³ recommends the use of ferrocyanide of potassium to a solution of any salts in the ore, to which there is no objection; but it should be pointed out that cobalt and nickel salts will give a greenish precipitate with this re-agent. The main objection to

¹ Roasting of Gold and Silver Ores, San Francisco, 1880.

² The Metallurgy of Gold, Rose, p. 229.

³ The Metallurgy of Gold, Eissler, p. 279.

Eissler's test is that it occupies some time and is not always performed properly, while, further, it only applies to soluble salts.

For a practical test, I consider the magnet gives a better clue to the state of the material in the furnace than any simple test recommended, the temperature at the time being high enough to decompose any ferrous sulphate. A sample can be readily taken from the furnace with a semi-cylindrical iron tube, emptied on a fire-clay tile, and the magnet run through it, when, if only a very small quantity adheres, the ore is sufficiently roasted.

Another test would be to make up a dilute solution of salt, sulphuric acid, and a few crystals of permanganate of potash, slightly stronger than that recommended by Professor Black. If it is decolourised on adding the roasted ore to it, then this is not sufficiently oxidised.

When the ore is removed from the furnace, the chloridising action of the salt, if added, still goes on, and the roasted material remains red-hot under a thin black crust for some hours. If this crust is broken, hydrochloric acid, volatile chlorides, and free chlorine escape. Tests were made of a considerable quantity of the ore, to determine whether any chloride of gold had condensed on the crust; but the results were negative. Neither could silver chloride be detected; but in the latter case the amount present must have been very small and might have escaped detection.

The ore remained on the brick cooling floor until almost cold; it was then moistened with water in sufficient quantity to make it adhere when pressed, but when released to fall to pieces. The smaller the quantity used the better for successful working.

The ore vats are lead-lined, with false bottoms and a gravel filter-bed below; both the filter-bed and the leaden sides are protected by wooden staves, which, together with all the internal woodwork, have been dried, warmed, and dipped in a molten paraffin bath.

The damped ore is fed into the vat through a sieve having 5 holes to the linear inch and is distributed evenly in layers with a garden rake, no packing being done; when full, the ore is pressed tightly around the edge of the vat to prevent chlorine escaping up the side, and the ore is raked away slightly from the

centre towards the circumference. If the false bottom is wet before charging the ore, dry ore should be sieved in until no more moisture is drawn up by capillary action.

The chlorine first used was generated from sulphuric acid and chloride of lime, but since it was impossible to get an even flow of gas, we discarded these and used liquid chlorine, prepared in Germany and exported in the usual steel cylinders, with $33\frac{1}{2}$ lbs. of chlorine in each. These work so well that, if the cost were not so great (chlorine 1s. 6d. per lb.) they would be largely used.

The chlorine from the cylinders is turned on and passed through a wash-bottle, so that the rate of flow can be regulated; from the wash-bottle it is conveyed to the centre of the false bottom of the vat.

The valve is turned so that chlorine can escape and pass through a half-inch pipe against a head of one inch of water at the rate of 6 bubbles per second. Yet at this speed it takes 6 hours to reach the surface of the ore. The cover is then lowered, a water-joint at the circumference of the vat making a perfect joint.

The valve is now turned down, so that a bubble may pass through the wash-bottle every 3 seconds, and this is continued until there is no back pressure. Stress was laid by early writers on chlorination about the necessity of separating hydrochloric acid out with wash-water, and speculations were common as to its injurious effects on the process. T. K. Rose¹ has shown the absurdity of the arguments brought forward.

It was found that during the passage of the ore the pipes became blocked up on cold nights, and, on investigation, the solid substance proved to be chlorine hydrate. The expansion of the gas on being released was sufficient to cause the cylinders to become frosted over in a few hours. It was also found that watery vapour diffused back into the chlorine, and this started to corrode the valves. These difficulties were overcome by using strong sulphuric acid in the wash-bottle.

The ore is allowed to remain for 48 hours in contact with the gas, and at the end of that time samples are taken from top to bottom, and the gold chloride is washed out. From 2000 to 3000

¹ The Metall. of Gold, p. 253.

grains of the leached sample are then taken and assayed, and if the returns show that from 2 to 4 dwts. are left in, according to the richness of the original sample, then the cover of the vat is raised and a spray of water under a pressure of about 20 feet from a rose is allowed to fall over the surface of the ore.

In this way most of the chlorine present is absorbed and carried down to the bottom of the vat. As soon as the liquid reaches the bottom, the lower tap is turned on and it escapes into the precipitating vat. Practically the first few gallons, when washing is done in this way, contain most of the gold.

When the surface of the ore, which has subsided by about a fifth of its height, is again above water, another shower is sprayed over it, and so on until the escaping liquid is free from gold.

By washing in this way, it will be found that wash-water less than half the bulk of the ore is sufficient to carry all soluble gold out; it also offers a further advantage: that should any solid reducing agent be present accidentally—say an iron bolt—almost the whole of the gold will be washed past without much danger of local precipitation; whereas, if the vat were filled in the orthodox way, undesirable secondary actions would go on for a considerable distance around the metal.

The auriferous solution is allowed to flow through an open-texture canvas bag, which serves to retain any sand, sulphate or chloride of lead, or other solid material which may have passed through.

The gold solution is tested with sulphate of iron in a porcelain basin, the slightest discolouration being made plain against a white surface.

Many authorities recommend stannous chloride, containing a small quantity of stannic chloride, as a more delicate test; but it is found in practice to fail, and is not so certain as the ferrous sulphate method.

The amount of chlorine used for each ton of ore was determined by weighing the cylinder before and after each operation, and it was found to vary from 6 lbs. to 10 lbs. of chlorine per ton of ore. On several occasions the ore was charged in hot, and it was found that more chlorine was required and the extraction performed in the same time as when cold. The escaping liquor contained much larger quantities of base chlorides than when cold.

It would therefore appear that, though gold is more readily attacked by hot chlorine than by cold, the same is the case with other materials also, and on a large scale; so that there is a positive disadvantage in charging the vats with hot ore. The extractions obtained from a large number of parcels varied from 93 per cent. to 97.6 per cent. of the gold contents.

Tests were always made in the laboratory on a few pounds of the roasted ore, to determine the amount of chlorine to be used, the time of contact to be allowed, and the extractions; and these afforded an infallible guide as to results on a larger scale, with the exception of time. It was found that while 24 hours might serve for a laboratory test, it took double that time to get the same result from some tons of material. It was also found that while the rate of dissolution went on rapidly at first, it became slower and slower, and in course of time practically ceased; so that there is a limit to the amount of gold to be extracted in a given time.

No difficulty has been experienced up to the present in treating the low-grade bullion mentioned before, although most writers have judged it would be difficult to deal with by chlorination.

When the whole of the wash liquor has been drained into the precipitation vat, there is usually enough lead present in solution to form a precipitate when sulphuric acid is added. Sulphate of iron solution and sulphuric acid (the latter to prevent the precipitation of basic sulphates) are added and stirred well; the precipitate formed—gold and sulphate of lead—falls rapidly, but is allowed to settle for 24 hours. The supernatant liquid is then tested, to see if any gold is still in suspension, and if there is none, the liquor is siphoned off, one leg of the siphon being attached to an india-rubber tube kept near the surface of the liquid by means of a float, and the other discharging into a mixture of sawdust and charcoal in an earthenware cylinder.

A solution of auric chloride is used to test the liquid draining off at different levels, as it sometimes happens that the upper layers may have excess of sulphate of iron and the lower ones still contain dissolved gold.

When the liquor has drained to within three inches from the bottom of the precipitate vat, the siphon is withdrawn, and the auriferous sludge washed out with a fine jet of water into a deep

earthenware vessel; it is allowed again to settle and the top liquor siphoned off, and, finally, the precipitate is emptied into a filter placed within a large funnel; after it has drained, the whole is dried in an iron dish, nitre sprinkled over it to help to oxidise the filter-paper, and then heated to burn out the organic matter.

The dried material is finally smelted down in a clay pot with the addition of borax. The gold thus obtained is almost pure. The slags are melted down with carbonate of soda, carbon, and litharge, and large cupels are made to hold the lead so reduced, which is then cupelled in the usual way.

In addition to the Plattner process, carried out as before described, a dilute solution of chlorine has also been used, but the extractions obtained were not quite so good as with the original method.

A trial was also made of the Etard-Black process, the details of which were kindly supplied to me by Mr. Stone, of the Government Analytical Laboratory. It was found that the quantities specified, viz.:—1st solution, water, 50 gals.; sulphuric acid, 14 lbs.; 2nd solution, water, 50 gals.; salt, 15 lbs.; permanganate of potash, 6 ozs.—gave too weak a solution to be used with ordinary roasted ores, but on increasing the amount of permanganate to about 24 ozs., and allowing the liquor to percolate slowly through the ore for 60 hours, 96 per cent. of the gold present was extracted. There does not appear to be any special advantages in the method over a dilute chlorine solution. It might be possible, however, to precipitate the gold on charcoal, and by oxidising the liquor again with permanganate, or other re-agents, it could be used over again. In that case the only waste would be due to the sulphuric acid used in dissolving base metals and the permanganate used each time.

Tests have also been made on the roasted ore with dilute cyanide of potassium solutions with highly satisfactory results, and it appears to me that, with proper handling, almost any roasted ore may be treated successfully with the cyanide solutions, with the further advantage that the silver is also recovered. Should the cyanide prove as effective as chlorine as a solvent for gold in roasted ores, then chlorination will soon be a method of the past.

The silver contents of our ores, when mixed, never amounted to more than 5 ozs. per ton, so that silver was not specially worth troubling over, though in the laboratory we could extract from the tailings about 60 per cent. of their contents with a hypo-sulphite solution, and 80 per cent., as well as a small quantity of gold, with a cyanide solution.

Repeated efforts were made to see if gold could not be recovered by amalgamation from the roasted material, but 75 per cent. was the utmost that could be obtained. The tailings from the chlorination vats were also tried, but only 25 per cent. of their gold would yield to amalgamation processes. It is exceedingly difficult to amalgamate very fine gold, even when it is free.

It is evident, though numberless modifications have been suggested, many of which have been carried out on Plattner's original method, that for simplicity and applicability to almost any ore it need never have been departed from.
